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Recent advances and challenges of current collectors for supercapacitors

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ABSTRACT

Global energy and environmental issues are driving the development of modern advances in efficient and environmentally friendly energy storage systems. Such systems must meet a range of requirements, which include high energy and power density, long service life, flexibility, industrial scalability, security and reliability. Progressive achievements in the field of energy storage are associated with the development of various kinds of batteries and supercapacitors. Supercapacitors are state-of-the-art energy storage devices with high power density, long lifespan, and the ability to bridge the power/energy gap between conventional capacitors and batteries/fuel cells. However, supercapacitors have limitations associated with low energy density, which can be solved by using various types of current collectors, since current collectors are one of the main massive components of supercapacitors. This review gives a complete understanding of the effect of current collectors on the actual performance and properties of supercapacitors. We reviewed current collectors based on carbon and metal-containing materials, and supercapacitor configurations to identify possible improvements in electrochemical performance in terms of specific capacitance, energy density, power density, service life and variability in their application.

1. Introduction

At present, the rapid pace of development of the world economy and global environmental problems require the development of new revolutionary strategies for solving energy problems [1–3]. Along with the limited supply of fossil fuels, there has been an increase in the number of electronic devices, which leads to an increase in energy demand. One of the solutions to these problems is the use of alternative energy sources, such as solar and wind, which are environmentally friendly sources of energy and are increasingly being used [4]. Meanwhile, their significant drawback is the dependence of energy production on external factors (presence or absence of sunny weather and wind). All this leads to the fact that alternative energy sources should be used in conjunction with modern technologies for efficient energy storage [5]. Modern advances in the commercial production of batteries and supercapacitors (also called ultracapacitors) are used not only to solve the problem of storing energy obtained from alternative sources but also in everyday human life. Currently, lithium-ion batteries are the main driving force in the energy storage sector. However, various types of batteries, such as lithium-ion batteries, have a low power density, which limits their use in various integrated power modules. Unlike batteries, which have a high energy density, supercapacitors are of particular interest in terms of their high power density and long life (Fig. 1a, b) [6,7]. At the same time, the use of various types of supercapacitors, such as electric double layer capacitors, makes it possible to obtain high power, while another type of supercapacitor, the pseudocapacitor, is best suited for obtaining high energy density.

Modern achievements in the field of supercapacitors, as well as for batteries, are mainly associated with active electrode materials such as activated carbon [8], graphene [9], carbon nanotubes [10,11], nanorods [12–14], MXene [15–17], and silicon oxide [18–20]. Therefore, many research and review articles on active electrode materials have been

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published in recent decades. Much effort has been put into reviewing the active electrode materials and electrolytes of supercapacitors. However, to the best of our knowledge, few reviews on current collectors have been published so far, and only a limited number of materials or designs are considered [21]. Current collectors, along with active electrode materials, are one of the main massive components (~15–20 % of the total weight of a supercapacitor cell), which significantly influence the gravimetric/volumetric specific energy density, power density, and long-term cycle stability. This brings us to the need for a more comprehensive overview of current collectors.

The key players in the supercapacitor market are the AVX Corporation, SPEL Technologies Private Limited, Tesla, Nippon Chemi-Con, Skeleton Technologies, CAP-XX, LS Mtron, Ioxus Inc., Evans Capacitor Company, KORCHIP Corporation and Panasonic Corporation. Most of these companies produce supercapacitors based on carbon electrodes with organic electrolytes and aluminum current collectors. Previous research studies on the supercapacitors with such configuration have shown that after a certain number of charge–discharge cycles the carbon layer often peels off from the smooth metallic current collector resulting in poor electrochemical performance. In order to avoid the peeling effect of the carbon layer from aluminum current collectors, recently manufacturers are starting to use modified current collectors such as etched aluminum foil and carbon-coated Al foil instead of smooth foils. Such modifications of the current collectors increases the strength of the bond between the active electrode material and the current collector and maintains a stable operation over hundreds of thousands of charge–discharge cycles [23,24]. The current collector is an indispensable component bridging supercapacitor and external circuit (power sources or electrical appliances), as well as the supporting substrate for loading the active electrode material, greatly influencing the capacity, rate capability, heat transfer property, and long-term stability of supercapacitors.

Compared to batteries, supercapacitors do not have a wide range of applications due to the two limiting factors of low energy density and high cost [25,26]. One possible solution to increase the energy density and reduce the cost of a supercapacitor is to develop new types or improve the existing types of current collectors along with active electrode materials used for supercapacitors. The growing interest in various materials used for supercapacitor current collectors is indicated by a number of research articles that have made it possible to consider the prospects and problems of choosing the type of material for supercapacitor current collectors [27–32]. All this indicates that the choice of current collector has a significant impact on the efficiency of both supercapacitors and various types of batteries. To the best of our knowledge, there are currently no review articles on this issue. From this point of view, we believe that today, the issue of a comprehensive and detailed analysis of materials used as current collectors for supercapacitors, as well as how and by what means their efficiency can be improved, is an acute issue.

2. The principle of operation of supercapacitors

Supercapacitors are electrochemical capacitors with a high energy density, which is hundreds of times greater than that of conventional electrolytic capacitors. Unlike conventional capacitors where charges are accumulated electrostatically, for supercapacitors, the accumulation of charges occurs as a result of electrostatic double-layer capacitance (EDLC) and electrochemical pseudocapacitance between the electrodes of the capacitor and the electrolyte [33]. These reactions are surface interactions, indicating that an increase in specific surface area leads to an increase in charge accumulation. Supercapacitors are systems consisting of two electrodes (anode and cathode), an electrolyte and a separator. Charge storage in the case of EDLC occurs predominantly at the electrode, and electrolyte ions are adsorbed at the electrolyte/electrode interface, while the separator acts as a semipermeable membrane that allows ion transport and prevents short circuiting of the device. The supercapacitor electrode includes a current collector and an active electrode layer coated on the surface of the current collector. The current collector serves to efficiently transfer electrons from the active material to external power sources or electrical appliances.

To date, there are three main types of supercapacitors that have different mechanisms of charge accumulation (Fig. 2a, b, c): electrostatic double-layer supercapacitors (EDLCs) [34], hybrid capacitors [35,36], and redox supercapacitors or pseudocapacitors [37,38]. For EDLCs, the accumulation of charges occurs as a result of the formation of an electric double layer due to electrostatic attractive forces that attract electrolyte ions to the surface of the electrodes. The electric voltage on the electrodes leads to the formation of one layer of charge, while to compensate for this layer, ions of opposite polarity from the electrolyte accumulate on the surface of the electrodes, forming a second ionic layer [39]. Between these two electrical layers are the solvent molecules (the Helmholtz plane).

Due to the significant difference in the geometric dimensions of electrons and ions, the density of the electron layer on the electrode surface is higher than that for the second ion layer. At the same time, the electrode potential changes linearly and becomes exponentially dependent when approaching the diffusion layer. This charge accumulation mechanism makes it possible to achieve a high speed for the charge/discharge cycle, while the service life is higher compared to other types of supercapacitors, and because no chemical reactions occur during the charge/discharge process, the structure of the electrodes remains unchanged. Thus, EDLCs are characterized by a long service life, and the specific surface area of the active material affects the capacitive characteristics of the supercapacitor.

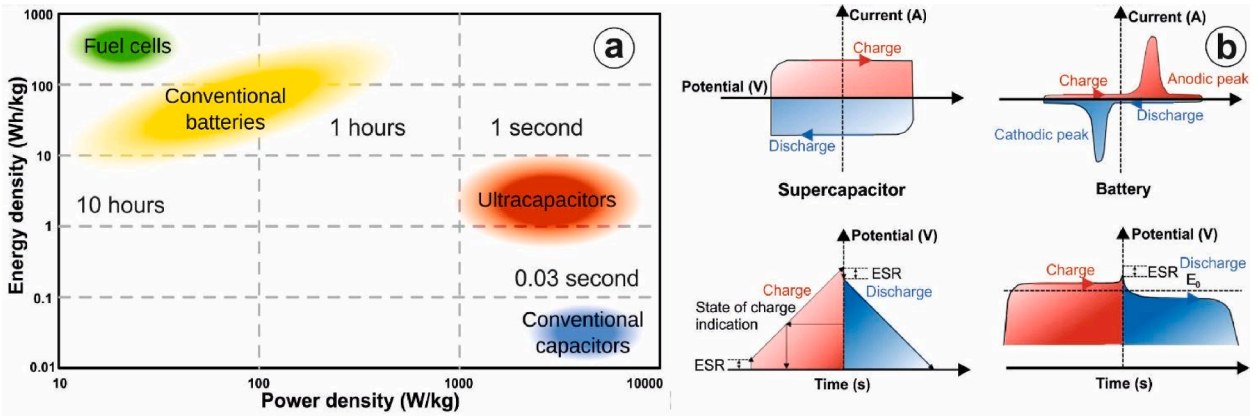

Fig. 1. (a) Energy and power density for different types of energy-storage devices (supercapacitors, fuel cells, conventional capacitors, and a typical battery); (b) Comparison of the electrochemical behaviour of a typical supercapacitor and a typical battery. Reprinted with permission from [22].

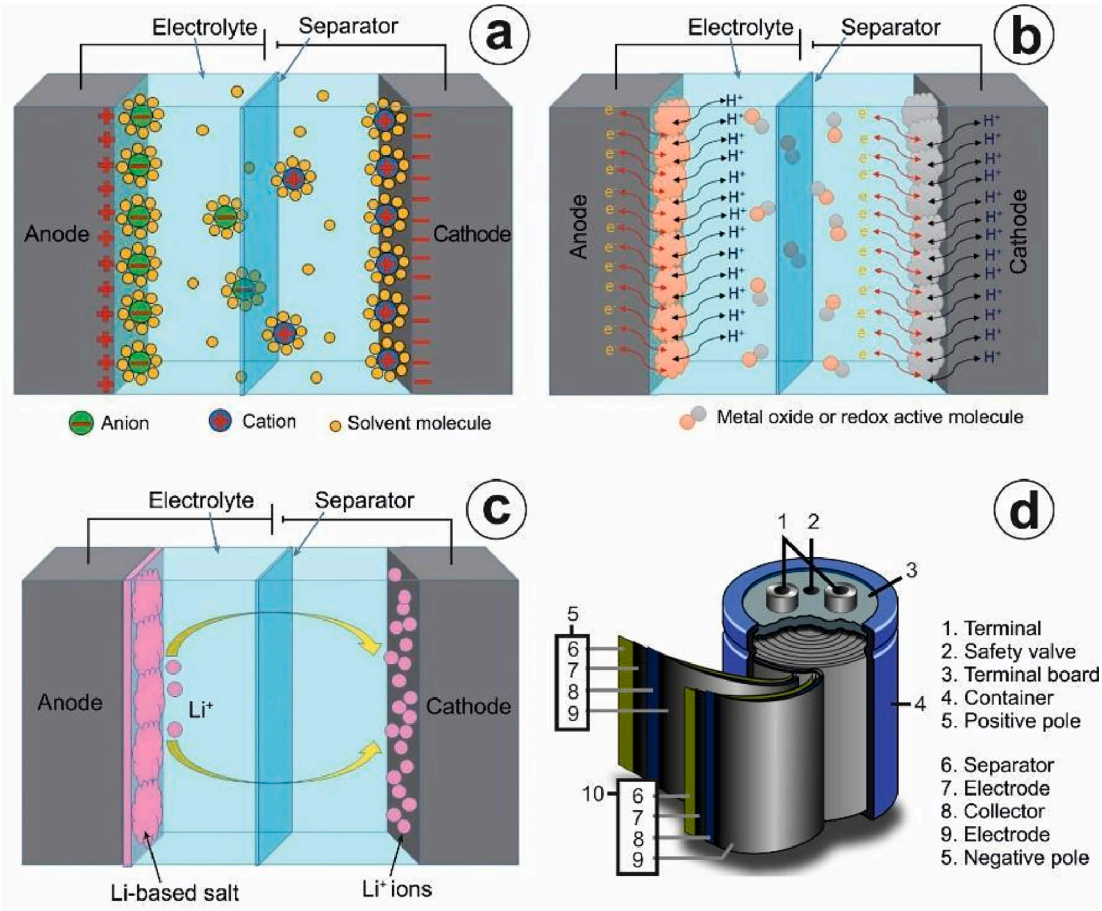

Fig. 2. Schematic illustration of (a) an electrical double-layer capacitor (EDLC); (b) pseudocapacitor (PC); (c) hybrid supercapacitor; (d) exploded view of a wound supercapacitor. Reprinted with permission from [40].

In contrast to EDLCs, the mechanism of charge accumulation for pseudocapacitors is the so-called surface Faradaic electron charge-transfer reaction [41]. These reversible reduction and oxidation reactions take place on the electrodes of the capacitor and largely determine its service life, since long-term chemical reactions during fast charge and discharge cycles can cause structural changes in the electrode [42]. The ongoing reactions are not accompanied by chemical transformations in the electrode material itself, but due to redox reactions, adsorption and intercalation, the process of charge transfer occurs. Therefore, materials with a mesoporous structure are preferable for the electrode material, which has a positive effect on the diffusion of electrolyte ions during charge transfer reactions [43]. Various types of materials are currently used as electrodes, including polymers with high electronic conductivity, metal oxides, and their composites [44–47]. Pseudocapacitors are characterized by high energy density and high capacitance values. Unlike EDLCs, pseudocapacitors have a fairly low power density.

Unlike EDLCs and pseudocapacitors, the hybrid supercapacitor has electrodes made from two different types of materials. In addition, the mechanism of charge accumulation includes both the formation of a double electric layer and Faradaic reactions [48]. This allows hybrid supercapacitors to have high energy density, low self-charging rate and high specific capacitance compared to symmetrical capacitors. The use of different materials as electrodes allows the use of the advantages of both EDLCs and pseudocapacitors, and the combination of these two charge storage mechanisms makes it possible to obtain capacitors with high energy density and power.

As a rule, in the manufacture of supercapacitors, special attention is given to the choice of material for the electrode, which mainly affects the parameters such as high specific capacitance, speed of charge and discharge cycles, and their stability. For example, carbon materials (activated carbon, graphene, carbon nanotubes, etc.) are widely used as electrodes for EDLCs, with transition metal oxides (RuO_2, MnO_2, CoO_x, NiO, Fe_2O_3) and reports on the use of MXene and various composites being based on them. In addition, manufacturers pay attention not only to the active electrode material but also to the current collector, which is one of the main key components of a supercapacitor that affects the overall specific parameters.

3. Main requirements for current collectors in supercapacitors

The efficiency of supercapacitors is determined by the choice of active electrode material, electrolyte, separator, and current collector. Each component plays a role and largely determines the characteristics of the supercapacitor. For example, the internal resistance of a supercapacitor is affected by the conductivity of the electrode material and the current collector, as well as the resistivity of the electrolyte and the thickness of the separator.

The ideal current collector should have high electrical conductivity, low contact resistance with the active electrode material, stable and strong bonding strength with the active electrode material, high specific surface area, high mechanical strength/modulus, low weight, high thermal stability, high electrochemical stability, and environmental and cost aspects must be considered. To date, metal current collectors (foil, porous metal) and current collectors based on carbon materials have been widely used in supercapacitors. However, there are general criteria for selecting current collectors, regardless of the properties of the supercapacitor, to ensure its high efficiency and stable operation:

1. High electrical conductivity. Current collectors provide efficient transfer of electrons to external circuits, which depends on their conductivity. In addition, the charge/discharge process may be accompanied by heat generation at the current collector with low conductivities. For the operation of a supercapacitor, not only the conductivity of the current collectors is important, but also the electronic resistance at the boundary between the current collector and the active electrode layer. The electronic resistance of current collect is typically negligible especially for metallic current collectors. Physico-chemical modification of the current collector surface and deposition of an additional intermediate layer between the active electrode layer and the current collector are the possible solutions for reducing the electronic resistance at the interface between the current collector and the active electrode layer.
2. Electrochemical stability. Insufficient resistance of current collectors to reactions occurring during the processes of charge and discharge can lead to an undesirable decrease in capacitance characteristics and a reduction in the service life of supercapacitors. The choice of current collectors and their modifications is carried out mainly depending on the type of electrolyte and the electrode material (and the method of its integration with the current collector).
3. Mechanical strength. Another important parameter is the mechanical strength of the current collector, as it maintains a stable connection between the electrodes and their integrity during charging and discharging. Current collectors are not only a charge transfer channel between the active electrode layer and the external circuit, but also a supporting carrier substrate, the mechanical properties of which are very important in the production of supercapacitor cells and the cell operation in harsh conditions.
4. Optimal density. An important factor is the optimal mass ratio of the active electrode material loaded on the current collector to the mass of the current collector, since the current collectors are an inactive component. However, current collectors account for about 15-20 % of the total weight of the supercapacitor. An increase in the ratio of the active electrode material mass to the current collector mass contributes to a decrease in the total mass of the supercapacitor and, consequently, to an increase in the specific energy density of the supercapacitor.
5. Sustainability and cost. The choice of material for the current collector also depends on its cost, availability, and possible recycling. These factors are of decisive importance not only in terms of commercial interest but also as an environmentally friendly recycling of used current collectors and the supercapacitors themselves.

4. Materials for current collectors

4.1. Carbon-based current collectors

Metal current collectors are widely used for the manufacture of supercapacitors; however, they have a number of significant disadvantages associated with corrosion, high interfacial resistance between the metal current collector and the active electrode material, the characteristic low gravimetric energy density of the entire cell and the impossibility of creating flexible supercapacitors, which are of great interest from the point of view of their potential applications [49–51]. On the other hand, unlike metal and metal-containing current collectors, the use of carbon materials as current collectors makes it possible not only to obtain flexible supercapacitors but also to reduce the interfacial resistance between the active electrode material and the current collector [52–54]. For example, the use of conductive carbon fibres as a current collector for EDLCs produced from polymerized ionic liquids (PILs) by electrospinning demonstrates excellent charge storage parameters (commercial Ketjen black carbon as the active material), superior to EDLCs based on carbon-coated aluminium foil [55]. At the same time, an EDLC with a current collector based on carbon fibres can operate at a current density of up to 40 A/g without a significant loss in capacitance, has high stability at high cell voltages and long cycles of work, and has good conductivity, comparable to a platinum current collector. At the same time, the disadvantage of such carbon fibres is the high cost and scalability of the method, which limits its possible commercial application.

Another promising carbon material for current collectors is conductive carbon paper. Yes, Peihui Luo and Lily Huang [56] demonstrated a simple method for making electrodes from graphene hydrogel and carbon paper, which was used as a current collector. Due to its high porosity and high electrical conductivity, graphene hydrogel electrodes using carbon paper as a current collector showed a high gravimetric capacitance of 294F/g at a current density of 1.18 A/g, which remained at 66 % (193F/g) even with increasing current density up to 28.24 A/g. Along with carbon paper, for the manufacture of disposable, nontoxic and flexible supercapacitors, graphite foil is also used as an effective current collector material (activated carbon as the active material). Maede Arvania and others [52] showed that graphite foil can be used as a current collector. However, studies indicate the effect of the porosity of the current collector on the chemical stability of the supercapacitor. For example, graphite foil (150 μm thick) showed high capacitance and low equivalent series resistance (ESR) but poor chemical stability. Presumably, this behaviour is explained by the influence of oxygen, which leads to oxidation and evaporation of the electrolyte, leading to a decrease in mass and an increase in leakage current.

Another carbon material used as a current collector is carbon nanotubes. Michel dos Santos Clem et al. [57] used poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) ink with the addition of multiwalled carbon nanotubes (MWCNTs). In this work, the composite ink was screen printed on filter paper and used as both an active electrode material and a current collector (Fig. 2a, b). Such a supercapacitor exhibits a capacity retention of up to 72 % after 1000 cycles with a specific capacitance of 20.3F·g^{-1} at a current density of 1 mA·g^{-1} at an energy density and power of 3.1 W·h/kg and 420 W/kg, respectively.

Printing technology is also being used for other types of carbon materials, such as graphene filaments as current collectors (graphite oxide is the active material). S.A. Baskakov et al. [58] demonstrated a supercapacitor based on graphene oxide, where a graphene filament was used as a current collector (Black Magic 3D) made in the form of a composite of polylactic acid (PLA) with the addition of carbon nanomaterials with high conductivity. On the other hand, the laser writing method is also used to make high-capacitance supercapacitors by converting graphene oxide into porous graphene films, which is current collector free active material [59]. Yes, Cho E - C et al. demonstrated a simple and scalable method for obtaining graphene-based supercapacitors with a large working area (4 × 4 cm^2) using an infrared CO_2 laser. Such a supercapacitor has reversible capacitances of 115.2, 97.0 and 78.4F/g at current densities of 0.5, 2 and 6 A/g, respectively, and only slight capacity loss after 4000 charge/discharge cycles and 2000 bending cycles, indicating high cycle life and mechanical stability (Fig. 3a-d). Although the use of graphene films makes it possible to achieve high capacitance values and good mechanical stability in comparison with metal current collectors, their use for the manufacture of supercapacitors with large areas is extremely difficult due to the use of lithography technology.

Graphene is also used as a current collector for supercapacitors. Pourjavadi et al. [60] used porous graphene as a current collector to accommodate carbon fibre-functionalized polyaniline to make a standalone supercapacitor electrode. The specific capacitance for this type of supercapacitor was 1.42F/cm^2 (710F/g) at a current density of 4 mA/cm^2 (2 A/g), while the capacitance of the electrodes decreased to 44.4 and 96, respectively, 8 % of the initial values after 1000 cycles, and lost ~ 30 % of its initial capacity at bending angles of ~ 120°, which once again indicates the prospects for the use of carbon materials for the production of flexible supercapacitors.

We should also note the difficulties associated with the multilayer

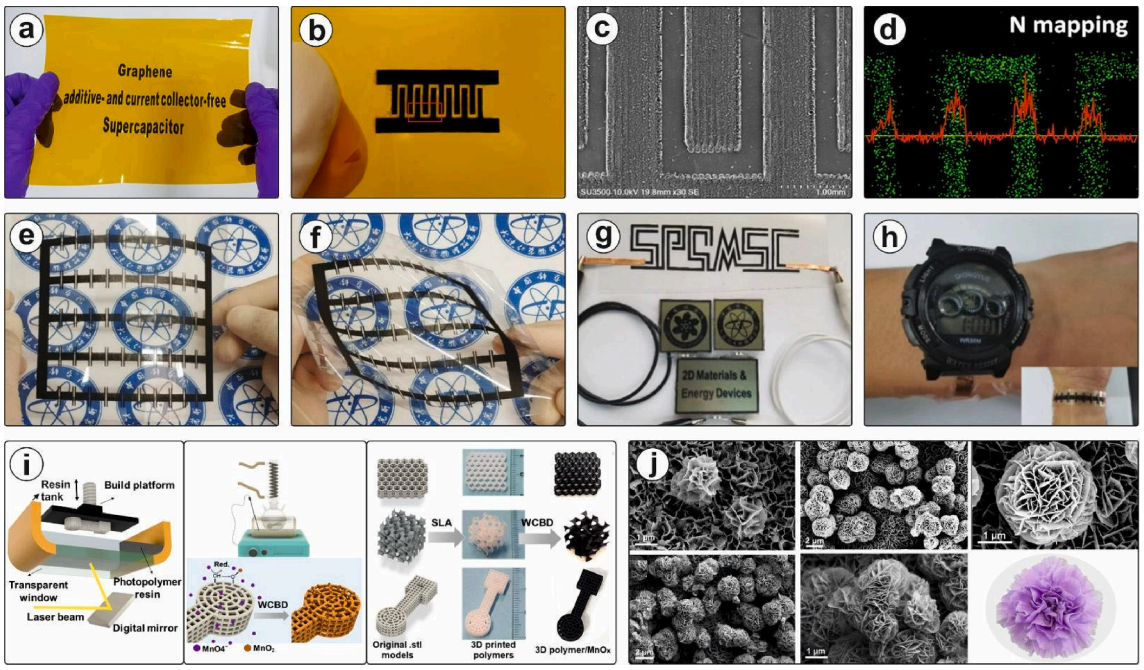

Fig. 3. (a) and (b) Digital photograph of polyimide-derived graphene (PIDG) patterned on a polyimide substrate; (c) and (d) SEM image and corresponding EDS mapping of the PIDG pattern; (e) and (f) digital images of screen-printed graphene-microsupercapacitors (SPG-IMSC); (g) Demonstration of a letter-shaped SPG-IMSC pack for powering 3 LCDs; (h) Demonstration of powering a sports watch with a SPG-IMSC pack connecting 8 cells in series; (i) Synthesis and self-assembly of the MnO_2 nanostructures onto the surface of the 3D-printed polymer network; (j) SEM images of 3D-printed polymer/MnO_x hybrid materials. Reprinted with permission from [59,61,62].

structure of supercapacitors, made in the form of a sandwich structure. The use of two substrates leads to a noticeable increase in volume and mass, which directly affects the gravimetric and volumetric capacities. This often results in the need for additional metal connections in the case of series and/or parallel connections of several supercapacitors to increase the voltage or capacitance. All this has led to the need for developing microsupercapacitors, which consist of interdigitated electrodes on a single substrate, obtained by screen printing. This structure provides a narrow space between the cathode and anode, which in turn leads to short circuit prevention and improved mechanical stability and flexibility. As evidenced by a study on the fabrication of graphene-based (actuating both as current collector and active material) tandem microsupercapacitors, which have a high capacitance (3.16 mF/cm^2) at a scan rate of 500 mV/s^1, and demonstrating outstanding cyclic stability with a capacitance retention of 91.1 % after 10,000 cycles [63]. At the same time, this screen printing method allows one to simultaneously print a large number of microsupercapacitors (from 100 to 1000) in a few seconds using graphene ink (actuating both as current collector and active material) [61]. At the same time, a tandem battery pack, consisting of 130 of these microsupercapacitors, allows one to obtain an output voltage of more than 100 V, which indicates excellent modularity (Fig. 3e-h). Screen printing allows the fabrication of stable supercapacitors, as evidenced by a systematic study of a large set of supercapacitors [64]. In this case, the current collectors and active layers in the supercapacitors under study were printed with paints from carbon materials such as graphite and activated carbon. It has been found that the best choices for using such devices are applications where low currents (<1 mA) are sufficient, such as in distributed sensors.

In addition to screen printing, 3D printing is also being used, allowing the fabrication of complex and adaptable 3D carbon structures in combination with bondless self-assembling nanostructures. At the same time, such supercapacitors have a good charge rate and demonstrate high gravimetric and surface capacitances (186F/g and 968 mF/cm^2, respectively) (Fig. 3i, j) [62]. On the other hand, as noted above, one of the limiting factors of traditional supercapacitors is the negative effect of the substrate mass, and the use of electrophoretic deposition on graphene airgel as a current collector (manganese and iron oxides were used as the active materials) makes it possible to create a bulk structure [65]. Such electrodes have a high gravimetric capacitance normalized to the total mass of the active material and current collector (mt) and amount to 143F/g. With such a structure, it is easy to avoid the excess mass of the current collector. When layer-by-layer deposition of the active material occurs on the current collector, some layer of the current collector will not interact with the active material but only the surface layer. This case is clearly demonstrated with metal current collectors, as evidenced by the electrochemical performance of nickel foam, which is superior to that of nickel foil. Therefore, metal-free supercapacitors with a carbon-based current collector have good flexibility, making them suitable for microelectronics applications. However, attempts to obtain an electrode with large areas and capacitance lead to capacitance losses and an increase in resistance, which makes them unsuitable when large capacitances and power are needed.

Table 1 summarizes data on carbon-based current collectors, including their fabrication methods; mechanical characteristics such as flexibility and stretchability; and electrochemical characteristics of these supercapacitors in terms of capacitance, impedance properties, rate capability and cyclic stability.

4.2. *Current collectors based on metal with various modifications*

Metal current collectors, in contrast to carbon and polymer materials, attract special attention due to their high conductivity and low cost. At the same time, they provide mechanical integrity and flexibility. However, as noted above, one of the main factors limiting their use is the corrosion of metal current collectors in a water-based electrolyte. At the same time, recent advances in the field of supercapacitors are mainly associated with aqueous electrolytes, which, in comparison with other types (organic electrolytes, ionic liquids and water-in-salt electrolytes), allow reaching high values of power density up to 10 kW/kg. An analysis of the available literature has shown that to solve this problem, methods

Table 1
Carbon-based current collectors.

Year	Current collector (CC)	Active material	Capacitance	Impedance (R_{ct} and R_s, Ohm)	Electrolyte	Method	Rate capability	Cyclic stability	Flexibility or Stretchability	Ref.
2019	carbon fibers	Ketjen black carbon		Impedance < 1.5	1 M Na_2SO_4	electrospinning and cross-linking	–	–	–	[55]
2020	carbon paper	graphene hydrogel	294F/g at 1.18 A/g, 193F/g at 28.24 A/g	R_{ct} < 2	1 M KOH	hydrothermal treatment (of active material)	66 % retention at 28.24 A/g	–	–	[56]
2020	graphite foil T68A	activated carbon	0.326	ESR = 1.3	NaCl:DI water = 1:5	printing technology	–	–	–	[52]
2020	graphite foil Sigraflex	activated carbon	0.361	ESR = 1.3	NaCl:DI water = 1:5	printing technology	–	–	–	[52]
2018	PEDOT:PSS/ multiwall carbon nanotube ink	PEDOT:PSS/ multiwall carbon nanotube ink	20.3F/g at 10^{-3} A/g	R_s = 58,3 R_{ct} = 2.762	gel-like electrolyte (PVA/ H_3PO_4)	screen printed	–	72 % after 1000 cycles	–	[57]
2017	polymer-nano-carbon	PANI	250F/g at 20 mV/s	–	1 M H_2SO_4	printing technology	–	–	–	[58]
2020	porous graphene-PEDOT	porous graphene-PEDOT	115.2 at 0.5 A/g, 78.4 at 6 A/g	R_{ct} = 66.8	1 M H_2SO_4	laser technology	–	slight losses after 4000 cycles	Slight losses after 2000 cycles	[59]
2018	porous graphene	carbon fibers@PANI	710F/g at 2 A/g, 1.42F/cm^2 at 4·10^{-3} A/cm^2	R_{ct} = 3	1 M H_2SO_4	chemical vapor deposition	–	96.8 % after 1000 cycles	–	[60]
2017	exfoliated (EG) planar graphene	exfoliated (EG) planar graphene	4.9 mF/cm^2 at 2 mV/s	ESR = 180	H_2SO_4/PVA	printing technology	64.6 % at 500 mV/s	91.1 % after 10,000	–	[63]
2017	mesoporous polyaniline graphene	mesoporous polyaniline graphene	7.6 mF/cm^2 at 2 mV/s	–	H_2SO_4/PVA	printing technology	–	80.9 % after 5000 cycles	–	[63]
2022	3D pyrolytic carbon	Mn_3O_4	186F/g or 968 mF/cm^2 at 0.5* 10^{-3} A/cm^2	Impedance > 140	1 M H_2SO_4	3D printing	–	>92 % after 5000 cycles	–	[62]
2018	reduced graphene oxide aerogel	MnO_2 nanotube	274 mF/cm^2 or 137F/g at 2 mV/s	Impedance > 20	0.5 M Na_2SO_4	hydrothermal method	above 50 % at 100 mV/s	–	–	[66]
2018	reduced graphene oxide aerogel	Fe_2O_3 nanotube	286 mF/cm^2 or 143F/g at 2 mV/s	Impedance > 20	0.5 M Na_2SO_4	hydrothermal method	above 50 % at 100 mV/s	–	–	[66]
2017	PF407C graphite	activated carbon	200 – 360 mF at 1 mA	ESR from 7.9 to 12.7	NaCl	printing technology	–	–	–	[64]
2018	paper-based expanded graphite (EG)	polypyrrole (PPy)	177.8F/g	R_s≈3	1 M H_2SO_4	brush-painting	from 510.3 to 329.7 mF/cm^2 retention from 1 to 10 mA/cm^2	>94.9 % after 5000 cycles	–	[67]
2021	graphite tape	MnO_2	577.5 mF/cm^2 or 91.7F/g at 0.5 mA/cm^2	R_s = 39.2	3 M LiCl	peeling off a thin graphite layer with a tape	about 33 % retention at 10 mA/cm^2	78 % after 5000 cycles	97 % after 1200 cycles of bending to 180°	[68]

* In the Tables 1 and 2, impedance means the sum of charge transfer resistance, solution resistance and diffusion layer. Impedance was used in the cases when authors provided EIS spectra but did not specify its parameters. R_{ct} – charge transfer resistance, R_s – solution resistance. The ESR was derived from IR drop of GCD curve.

are used based on the use of expensive corrosion-resistant metals (platinum, nickel, stainless steel), conductive composites based on metals and carbon materials, and modification of metal current collectors by physical and chemical treatment (laser irradiation, chemical and electrochemical deposition) (Fig. 4) [69]. In addition, research in this field shows that after a certain number of charge–discharge cycles, the carbon layer often peels off from the untreated smooth metallic current collector in activated carbon-based supercapacitors with organic electrolytes resulting in declined electrochemical performances. All these publications indicate the prospects for improving metal current collectors by modifying both physicochemical methods and carbon materials, which help suppress corrosion, improve interfacial contact and reduce internal resistance.

Ordinary graphite can be used as a carbon material, the hydrophobic layer of which is deposited on aluminium foil to improve the interfacial contact between the active material and the current collector [70]. The deposited graphite layer has high adhesion and highly ordered packing on aluminium foil, which makes it possible to create a strong interfacial contact between the active material layer and the modified current collector without voids. In addition, graphite helps to suppress the formation of a resistive oxide film on the surface of the aluminium foil and suppresses corrosion, which makes it possible to achieve high capacitance values and improved cycle life. The surface of aluminium current collector was treated by laser which reduced oxygen content and lead to a better interaction with active material. 95 % capacitance retention was demonstrated by the aluminium current collector protected with

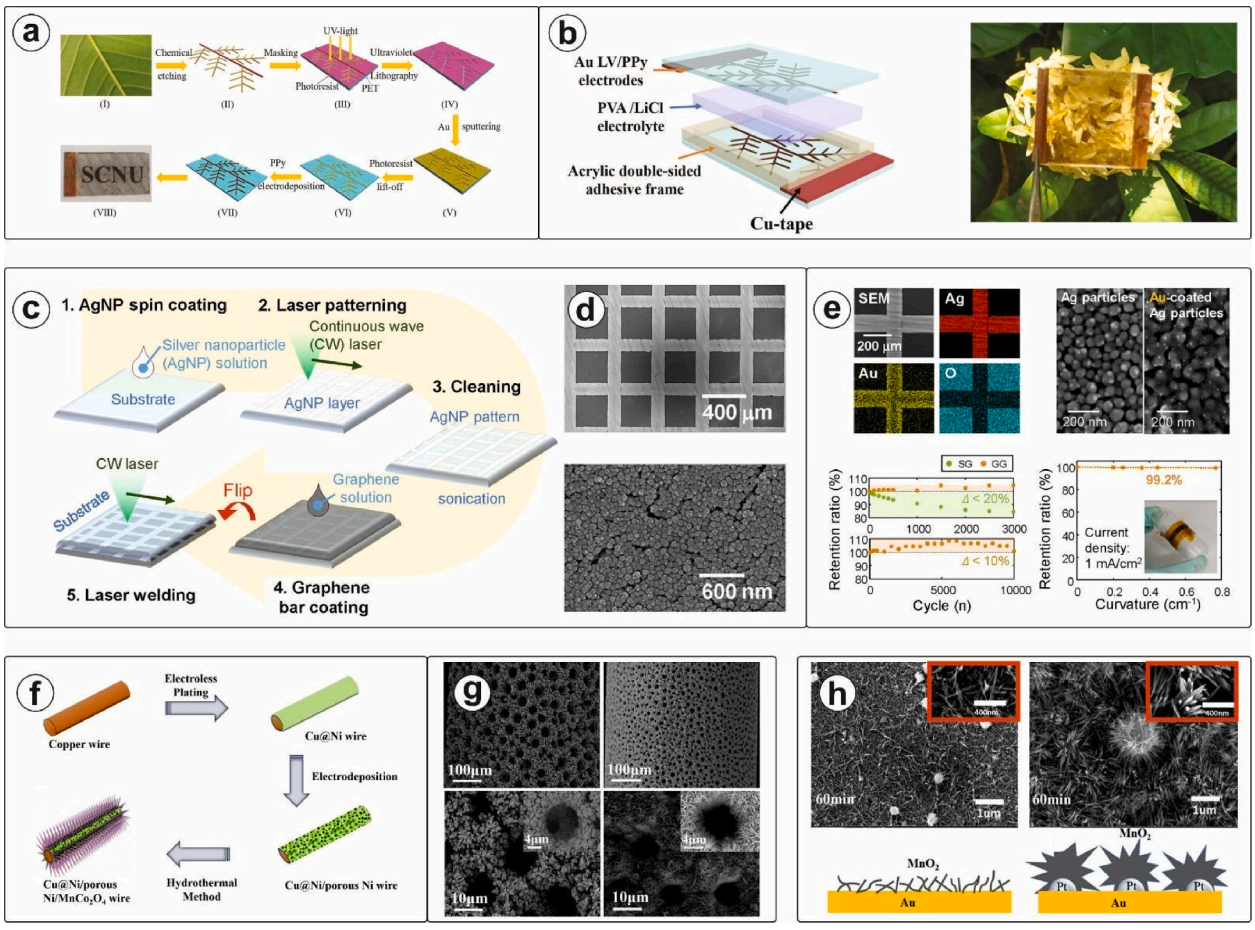

Fig. 4. a) Schematic illustration of the PPy/Au LV network electrode fabrication process and of the device structure; b) photograph of supercapacitor, demonstrating high transparency; (c) schematic of the graphene electrode fabrication process; (d) the Ag grid film, and the sintered Ag nanoparticles; (e) SEM and EDS mapping images of the Au grid and retention rate by mechanical bending of the GG sample (inset: photograph of the Au/Ag grid supercapacitor bent around a lab vial); (f) schematic illustration for the fabrication of Cu@Ni/porous Ni/$MnCo_2O_4$ electrodes; (g) SEM images of 3D porous Ni skeletons of Cu@Ni/porous Ni, and Cu@Ni/porous Ni/$MnCo_2O_4$; (h) SEM images of nanostructured MnO2 under 80 °C with different reaction times on Au film and Pt@Au film; schemes of MnO2 nucleation model on Au substrate and on Pt@Au substrate. Reprinted with permission from [69,78,82,83].

commercial graphite ink Acheson Electrodag 965SS after 950 days of test [52]. There are several research papers in which the authors have used commercial carbon-coated aluminum foil, also called conductive coated aluminum foil, as a current collector to improve the performance of supercapacitors [71,72].

Carbon-coated aluminum foil can maintain long-term electrochemical stability on a platform with a higher voltage than pure aluminum, can withstand long-term immersion in electrolyte, has excellent surface contact ability, can provide excellent interface conductivity, can withstand the stress generated during the long-term cycles of the supercapacitor.

Along with graphite, the use of carbon nanofibres has also been reported, which, due to their high surface area and simple preparation methods, are attractive for modifying metal current collectors. X. Chen et al. demonstrated a simple method for obtaining the electrode based on the electrospinning of MnO-polymer nanofibres followed by electrochemical 3D printing of a strictly controlled current collector of copper layer onto a composite [73]. This leads to a significant increase in the electronic conductivity of the electrode (by>360 %) and an increase in specific capacitance (by 110 %), which is presumably based on a decrease in interfacial resistance due to carbon fibres. Graphene oxide is also used to create modified composite current collectors with metals. One such example is the GO@AgNW (active material is activated carbon) flexible current collector composite, which is synthesized by sputtering silver nanowires onto the surface of graphene oxide [74]. This approach makes it possible to achieve not only high corrosion resistance due to the presence of functional groups in graphene oxide, but at the same time, such a supercapacitor demonstrates a retention of 70 % after a cyclic tensile test (~10,000 cycles, 40 % elongation) and 60 % after an additional cyclic charge–discharge test (3000 cycles).

Another modification method is the physical treatment of metal current collectors; for example, picosecond laser action on aluminium current collectors contributes to an increase in the capacitance of supercapacitors up to 110.1F/g, which is due to the removal of the oxide layer and an increase in contact with the electrode [32]. At the same time, such processing of the current collector led to an improvement in the cyclic stability of the supercapacitor due to a stronger contact with the electrode and prevention of delamination. Electrochemical etching modifications have also been reported for nickel current collectors, which, although characterized by high power density, fast charge/discharge cycles and long life, have a flat surface that leads to cyclic instability. Improving its characteristics is possible by modifying its surface structure to create a larger area of contact with the electrode material. This is evidenced by the studies carried out in [75], which show that nickel foam has higher electrochemical characteristics, reaction reversibility, higher pseudocapacitance and weaker polarization in comparison with the nickel grid. A simple electrochemical etching method can be used to achieve these goals, while functionalization of the surface of the nickel current collector can significantly increase the capacitance characteristics of commercial electrode material (activated

carbon) up to 210F/g at a current density of 0.5 A/g and cycle stability of 89 % after 10,000 cycles [76].

Nickel can also be used as nanospheres up to 400 nm in diameter chemically deposited on the surface of filter paper, which exhibits excellent electrical and mechanical properties: the surface resistance is 2.7 O/cm2 (Ro = 0.8 O/cm2) after 5000 bending cycles, and the mass density is only 0.35 g/cm3 [77]. The porosity achieved due to the nickel metal layer provides a large area of contact with the active material, which has a positive effect on the capacitance characteristics. In contrast to the thin layer of nickel nanospheres, dense double layers are advantageous in terms of the high corrosion resistance of the nickel coating. This kind of coaxial composite current collector has excellent flexibility and mechanical strength and allows us to obtain a high capacitance of up to 20.6 mF/cm and an energy density of 4.8 μWh/cm at a power density of 32.25 μW/cm (Fig. 4f, g) [78].

Unlike nickel-plated current collectors, the use of three-dimensional (3D) porous nickel coated with nickel hydroxide has a number of advantages that make it possible to achieve the theoretical capacitance and high-speed performance of supercapacitors. The nickel hydroxide layer can reduce the pore size of commercial nickel foam from 300 μm to 10–20 μm, which leads to a noticeable improvement in the performance of the supercapacitor, while it demonstrates a maximum capacitance of 3637F/g (active material is $Ni(OH)_2$) at a current density of 1 A/g and retains 97 % capacitance at a high current density of 100 A/g with a cyclic stability of>80 % after 10,000 cycles [79]. All these works point to the obvious influence of micro- and nanostructures of the current collector on the electrochemical properties of the supercapacitor. A striking example is a massive current collector consisting of nickel nanorods, i.e., the active material is in a thick layer of the current collector. This structure makes it possible to create numerous conducting channels, which significantly reduces the contact resistance of the thick electrode layer at their interfaces. At the same time, such current collectors have a high specific capacitance exceeding more than sixfold that of nickel foil, which is 795F/g for an NN@MnO2 electrode with a MnO2 mass load of 0.054 mg/cm2 [80]. At the same time, an increase in the electrode load by a factor of 20 leads to a decrease in the gravimetric capacitance to 326F/g, but the areal capacitance increased>8 times; this behavior indicates the important role of interfacial contacts between the active material and the current collector. When the active material is a thick layer, the structure of the current collector must be selected accordingly, that is, having a large specific area of interfacial contact. However, massive current collectors and thick layers of active material have limitations associated primarily with their flexibility and mechanical strength, as well as low energy density.

It should be noted that a new trend in the field of current collectors is the use of paper as a flexible and efficient current collector due to its low cost, flexibility and the possibility of its modification with metals by various methods. Another trend is the creation of transparent supercapacitors that replicate the structure of the bioinspired quasi-fractal structure of leaf venation (LV), where a metal network acts as a current collector (Fig. 4a, b) [81]. Such supercapacitors have excellent specific capacitance, which is 5.6 mF/cm2 with a transparency of 45 % [82]. Flexible and transparent supercapacitors are of particular interest for creating next-generation electronics for various applications, such as projection displays, biological sensors and smart devices [83]. Large-scale production technologies for such transparent intelligent supercapacitors can be based on the use of a flexible and ultralight current collector made of a 3D nickel microgrid and highly active Ni-Co bimetallic hydroxide as an active material [84]. Another example of a current collector for a transparent supercapacitor is a lithographed silver mesh, which exhibits high optical transparency (~80.58 % at 550 nm), flexibility and stability [85]. Meanwhile, transparent supercapacitors are characterized by low capacitance values, and their increase leads to a decrease in the optical transparency of the device, which limits their practical application.

Table 2 summarizes data on metal current collectors, including their fabrication methods; mechanical characteristics such as flexibility and stretchability; and electrochemical characteristics of these supercapacitors in terms of capacitance, impedance properties, rate capability and cyclic stability.

5. Conclusions

In this review, we have detailed and summarized the latest advances in the development and application of current collectors for next-generation supercapacitors with longer lifetimes, greater environmental friendliness and lower costs, as well as the ability to match properties depending on the application. To achieve these goals, it is necessary to pay attention to the fact that the current collector does not increase the total capacitance of the supercapacitor but allows the capacitance of the active material to be maximized. At the same time, a well-designed structure of the current collector and the electrode as a whole improves the energy and power density of the supercapacitor. Over the past five years, in the research and development of current collectors, the attention of the authors has been directed to obtaining micro, flexible, stretchable, wearable and transparent supercapacitors where large energy capacities are not needed. To improve properties such as conductivity, power, rate and cycling stability, light weight and increased energy density are mainly dependent on the current collector along with the active material. Thus, studies of the influence of the current collector structure on the electrochemical properties of supercapacitors indicate that a nanostructured current collector has a number of advantages associated with a high specific surface area and electrical conductivity, which reduces the resistance to diffusion and ion transport in the electrolyte. However, the latest development trends are related to 3D structures, where the current collector and active material together form a complete 3D electrode. As with other energy storage devices, supercapacitors are seeing a shift towards microsupercapacitors, which are complex circuits that combine up to 130 supercapacitors into a single circuit that outputs>100 V. Thus, for the development of a new generation of supercapacitors, it is necessary to conduct research on the materials and structures of current collectors in the following areas:

1. Despite numerous studies on the use of current collectors based on carbon materials and various polymers, which were considered as an alternative to metal current collectors, the problem of ensuring full contact between the current collector and the active material has not yet been solved. From this point of view, we believe that the tendency to create an integral three-dimensional electrode that will act as both a current collector and an active material is a possible solution to ensure good contact between the current collector based on carbon materials and the active material.
2. On the other hand, metal current collectors, unlike carbon materials, attract special attention due to their high conductivity and low cost; at the same time, they provide mechanical integrity and flexibility. However, their use in water-based electrolytes limits metal current collectors. In the literature, there has been an increase in research aimed at improving metal current collectors by modifying both physicochemical methods and carbon material integration, which help to suppress corrosion, improve interfacial contact and reduce internal resistance. The use of methods such as laser irradiation and chemical and electrochemical deposition makes it possible to create uniform layers of a given thickness and, accordingly, masses, providing high porosity and improved adhesive properties.

CRediT authorship contribution statement

Alisher Abdisattar: Conceptualization, Methodology, Writing – original draft, Investigation. **Mukhtar Yeleuov:** Data curation, Supervision, Writing – review & editing. **Chingis Daulbayev:** Conceptualization, Methodology, Writing – original draft, Investigation, Writing – review & editing. **Kydyr Askaruly:** Supervision, Validation. **Aidos**

Table 2
Current collectors based on metal with various modifications.

Year	Current collector (CC)	Active material	Capacitance	Impedance (R_{ct} and R_s, Ohm)	Electrolyte	Method	Rate capability	Cyclic stability	Flexibility or Stretchability	Ref.
2021	Al graphite	activated carbon	105.3F/g at 10 mV/s, 102.4F/g at 1 A/g	$R_{ct} \approx 0.4$	1 M Na_2SO_4	roll-to-roll coating technology	74 % retention for 100 mV/s, 86 % retention at 20 A/g	almost 100 % after 10,000 cycles	–	[68]
2019	Cu	manganese@carbon nanofibers	208F/g at 5 mV/s	$R_s + R_{ct} < 9$	0.25 M bis (trifluoromethane) sulfonimide lithium	electrochemical 3D printing	–	–	–	[70]
2020	graphene oxide nano flakes@silver-nanowire	graphene hybrid hydrogels	108F/g at 3 A/g	–	0.5 M H_3PO_4	alternating sequence of spray-coating	–	–	70 % of retention after 10,000 stretching cycles with 40 % elongation	[73]
2018	Al	activated carbon	110.1F/g at 0.1 A/g	$R_{ct} = 7.3$	1 M tetraethylammonium tetrafluoroborate in acetonitrile	picosecond laser processing	–	91.5 % retention after 10,000 cycles	–	[74]
2019	Ni	activated carbon	210F/g at 0.5 A/g	$R_{ct} = 0.71$	6 M KOH	electrochemical etching process	83 % retention at 20.0 A/g	89 % after 10,000 cycles		[76]
2019	Ni paper	MnO_2	1095 mF/cm^2 at 1 mA/cm^2	$R_s \approx 1.0$ $R_{ct} = 5.5$	1 M Na_2SO_4	electroless deposition	–	97.3 % after 1000 cycles; 73 % after 2000 cycles.	sheet resistance is 2.7 Ω/cm^2 ($R_o = 0.8$ Ω/cm^2) after 5000 bending cycles	[77]
2018	Cu@Ni /porous Ni	$MnCo_2O_4$	1280 mF/cm^2 at 5 mA/cm^2	$R_s = 1.4$, Impedance < 15	2 M KOH	electroless plating and hydrogen bubble dynamic template electrodepostion	–	–	–	[78]
2017	3D nickel	$Ni(OH)_2$	3637F/g at 1 A/g	$R_s = 1.32$, $R_{ct} = 0.31$	1 M KOH	electrodeposition	97 % retention at 100 A/g	80 % after 10,000 cycles	–	[79]
2017	nickel nanorod arrays	MnO_2	795F/g or 42 mF/cm^2 at 5 mV/s	$R_{ct} = 3.25$, Impedance > 30	1 M Na_2SO_4	anodic aluminum oxide template	–	–	–	[80]
2019	Au leaf venation	Polypyrrole	13 mF/cm^2, at the current I = 0.1 mA	Impedance < 5	1 M LiCl	leaf venation template	61.7 % retention from 0.1 to 1 mA	93 % after 1000 GCD cycles	93.9 % capacity retention for 500 bending cycles	[82]
2021	3D Ni micromesh	Ni–Co bimetallic hydroxide	75.58 μA·h/cm^2 at 1 mA/cm^2	ESR = 0.75 Impedance > 6	2 M KOH	photolithography and electrochemical deposition	60.6 % capacity retention from 1 to 50 mA/cm^2	88.7 % after 2500 cycles, 81.4 % after 6000 cycles		[84]
2017	Ag-grid@PET	PEDOT: PS	2.79 mF/cm^2 at 0.01 V/s, 0.85 mF/cm^2 at 1.00 V/s	$R_s \approx 2$	PVA/H_3PO_4	lithography and scrap techniques	–	92 % after 10,000 cycles	97.4 % after 1000 cycles	[85]

Tolynbekov: Supervision, Validation. **Azamat Taurbekov:** Supervision, Validation. **Nikolay Prikhodko:** Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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